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# Hydrothermal conversion of Cs-polluted soil into pollucite for Cs immobilization

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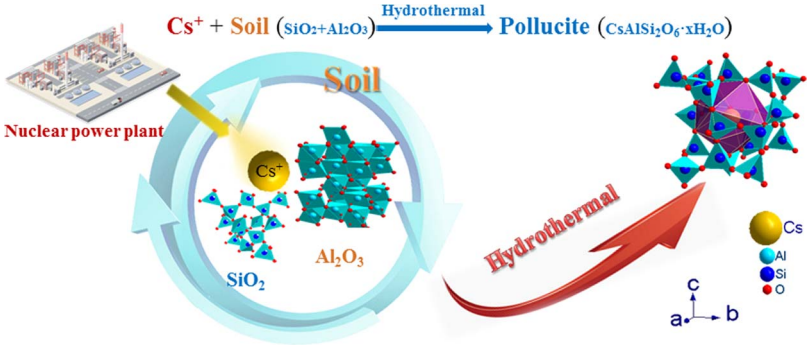
## GRAPHICAL ABSTRACT




## ARTICLE INFO

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## ABSTRACT

To deal with the treatment of huge amounts of Cs-polluted soil from the first nuclear power plant in Fukushima (Japan), a low temperature hydrothermal technology has been developed to convert polluted soil into pollucite for the in-situ immobilization of Cs. The results show that pollucite could be synthesized with a wide range of Cs content using a short curing time (2 h) or low curing temperature (160 °C). However, a higher curing temperature or a longer curing time seems to favor the formation of more pollucite. With the addition of $Ca(OH)_2$, a tough pollucite body could be synthesized, and the strength enhancement is mainly due to calcium silicate hydrate (C-S-H) formation. This also suggests that the hydrothermal technology has great potential for the direct immobilization of polluted Cs with a tough synthesized pollucite body, similar to cement or glass solidification of nuclear waste. The extended X-ray absorption fine structure (EXAFS) results reveal that the polluted Cs is immobilized into the structure of the synthesized pollucite rather than physically adsorbed in the pores. The leaching test results show that the amount of Cs leached from the synthesized specimens is very low ($2.43 \times 10^{-3}$ g·m$^{-2}$·d$^{-1}$ and $6.46 \times 10^{-4}$ g·m$^{-2}$·d$^{-1}$), even lower than that of the reference hollandite-rich synroc ($2.0 \times 10^{-2}$ g·m$^{-2}$·d$^{-1}$). As such, the hydrothermal synthesis of pollucite using only Cs-polluted soil for immobilization of polluted Cs, may provide a new technology for the treatment of Cs-polluted soil.

## 1. Introduction

With energy consumption increasing year by year, nuclear energy is rapidly becoming indispensable due to the advantages of negligible greenhouse gas emissions, energy-efficiency, and long term economic competitiveness, etc. Nuclear energy currently provides 7% of global

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primary energy (17% of electricity) [1]. However, nuclear power generation is accompanied by the production of radioactive waste which must be isolated and confined in appropriate disposal facilities until it no longer poses a threat. Traditional methods of disposing radioactive waste rely on the solidification of nuclear waste with cement [2,3], glass [4], resin [5–7] or another matrix.

Furthermore, radioactive leakage due to nuclear accident poses a threat to human well-being [8]. For example, radioactive Cs released from the Fukushima Daiichi nuclear power plant in 2011 resulted in significant amounts of soil pollution (~29 million cubic meters) causing serious damage to the environment [9] and human health [10]. Traditional methods for the treatment of radioactive waste, such as cement and glass solidification processes, are clearly unsuitable for significant Cs-polluted soil treatment because a large amount of solidification materials (cement and glass) are also required.

The artificial rock method is now considered to be the optimal strategy for the immobilization of radioactive waste [11–14]. Pollucite, which possesses a high cesium content and good thermal stability [15–17], is considered to be a promising material for cesium immobilization. Pollucite is synthesized via a sintering method at approximately 1000 °C in air [18–20] and as a result, radioactive materials volatilize and the equipment is easily corroded. A low temperature hydrothermal technology has therefore been used to synthesize pollucite. For example, pollucite has been hydrothermally prepared at 240–300 °C over a period of hours/days from clinoptilolite [21].

We have also synthesized pollucite using a hydrothermal method, and in our previous studies, chemical reagents were used to hydrothermally synthesize pollucite in order to reveal the differences between pollucite and analcime [22]. Furthermore, in order to verify the possibility of synthesizing pollucite from polluted soil to immobilize Cs, metakaolin was first employed [23]. If the Cs-polluted soil could be converted to pollucite, this technology could be applied to the treatment of vast amounts of Cs-polluted soil. However, research that uses soil to synthesize pollucite for immobilization of Cs under hydrothermal conditions has not been widely reported. In addition, with regards to the aforementioned studies concerning the hydrothermal synthesis of pollucite, a number of other reagents had to be introduced which undoubtedly increases the amount of treatment materials. With regards to the nuclear accident in Fukushima (Japan) where large amounts of Cs-polluted soil was produced, the synthesis of pollucite via Cs immobilization on only polluted soil remains highly challenging (in the absence of any base solidification materials).

The present work is aimed at: (1) assessing how to synthesize pollucite with only soil; (2) investigating the Cs immobilization mechanism and the coordination environment for Cs in the structure of the pollucite using EXAFS analysis; and (3) verifying the immobilization stability of Cs on the synthesized pollucite via leaching tests.

## 2. Material and methods

### 2.1. Material

Soil obtained from Shanghai (China) was used as raw material. The chemical composition of the soil was determined using X-ray fluorescence (Table 1) which showed high contents of $SiO_2$ and $Al_2O_3$ with only trace amounts of other oxides, suggesting the probability that the soil can be converted to pollucite. The mineral composition, determined by XRD (Fig. 1), shows that the main constituent of the soil is Quartz ($SiO_2$) with small amounts of Albite, Corrensite, Muscovite, Margarite, and Montmorillonite.

The soil was ground in a ball mill to pass 120-mesh screen, and its particle size distribution, measured by a laser particle-size analyzer, as shown in Fig. 2, in which the average particle sizes D (50) of the soil were 18.82 μm.

Analytically pure $Ca(OH)_2$, $Al_2O_3$ and CsOH were purchased from Sinopharm Chemical Reagent Co., Ltd. and Shanghai China Lithium Industrial Co., Ltd respectively. $^{133}Cs$ was used as a substitute of the radioactive $^{137}Cs$ in this study.

**Table 1**
Chemical composition of soil.

| Composition | Content/% |
|---|---|
| $SiO_2$ | 68.9 |
| $Al_2O_3$ | 12.8 |
| $Fe_2O_3$ | 4.19 |
| CaO | 2.88 |
| $K_2O$ | 2.44 |
| MgO | 2.08 |
| NaO | 1.33 |
| $TiO_2$ | 0.88 |
| $P_2O_5$ | 0.25 |
| $SO_3$ | 0.17 |
| MnO | 0.09 |

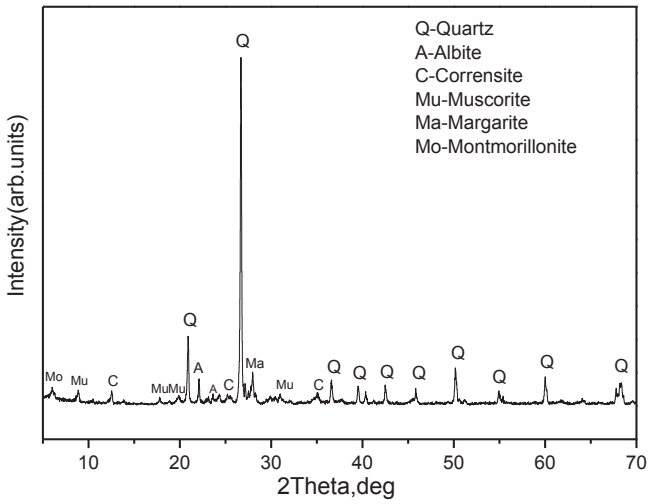


**Fig. 1.** XRD phase composition analysis of soil.

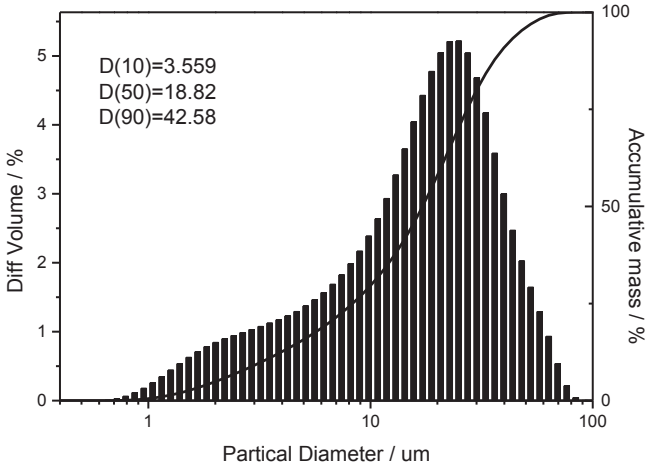


**Fig. 2.** Particle size distribution of soil.

### 2.2. Hydrothermal synthesis

Ground soil mixed with alumina at certain molar ratios of Al/Si were used as starting materials. The starting materials were initially mixed with 5 mass% CsOH solutions at Cs/Al/Si molar ratios of 1/1/5, 1/1.5/5, 1/2/5, 1/2.5/5, respectively, in order to synthesize pollucite. The mixtures were compressed in a stainless rectangular-shaped mold (40 mm × 15 mm × 45 mm) at a pressure of 30 MPa. The demolded